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A first report on ternary complex formation between *p*-sulfonatothiacalix[4]arene, tetramethylammonium ion and gadolinium (III) ion in aqueous solutions

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Abstract

The three ternary Gd^{3+}–*p*-sulfonatothiacalix[4]arene–tetramethylammonium complexes formed in aqueous solutions at pH 4–10 have 1:1:1 stoichiometry and enhanced stability due to Gd^{3+} coordination via phenolate groups at the lower rim and tetramethylammonium included into the cavity through the upper rim.

Keywords: Ternary complex; Gadolinium (III); *p*-Sulfonatothiacalix[4]arene; Tetramethylammonium ion

The development of lanthanide-containing water-soluble aggregates is becoming increasingly important during recent decades due to outstanding magnetic, optical and biomimetic properties of lanthanide ions [1]. Formation of such aggregates on the basis of calix-like ligands in solid state is well documented [2]. We have recently shown [3] that replacement of small guest cations (e.g., *N*-methylpyridinium or tetramethylammonium) by the long-chained (*N*-cetylpyridinium or *N*-cetyltrimethylammonium) ions in their ternary complexes with sulfonatomethylated calix[4]resorcinarene and Gd^{3+} ions in aqueous solutions leads to the reversible formation of Gd^{3+}-containing assemblies.

Thus, inclusion of hydrophobic organic ions into the cavity of calixarene can promote self-assembling of calixarene-based metal complexes. In this context, *p*-sulfonatocalix[4]arene (CAS) and *p*-sulfonatothiacalix[4]arene (TCAS) (Scheme 1) are of special interest, because they form inclusion complexes with organic cations [4,5] and possess pH-dependent complexability towards metal ions [6,7].

In particular, they bind lanthanide ions via sulfonate groups of the upper rim in acidic [6] and via phenolate groups of the lower rim in alkaline media [7,8]. That is why, we have extended the investigation of lanthanide-containing supramolecular systems to the water-soluble calixarenes. Assuming that from the viewpoint of the affinity of the cavity to organic substrates as well as the complexability of the phenolic rim towards lanthanide ions TCAS can surpass CAS [9], the first was chosen as a ditopic receptor for ternary complex formation. Supramolecular packing in the solid state of TCAS ternary complexes with DMSO and Ln^{3+} ($Ln^{3+} = Gd^{3+}$, Nd^{3+}) ions was estimated from X-ray data of crystals obtained from acidic solutions, where lanthanide ions are coordinated via sulfonate groups [10]. Meanwhile,

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